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Intramolecular Participation in Hypervalent lodine Oxidation. The Synthesis of Coumaran-3-ones, Aurone, and Isoaurone

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Oxidation of *o*-hydroxyphenyl alkyl ketones with PhI(OAc)₂/KOH–MeOH leads to 2,2-dimethoxycoumaran-3-ones which in the case of *o*-hydroxy- α -phenylpropiophenone offers a convenient route to aurone and isoaurone.

Oxidation of various acetophenone derivatives with PhI- $(OAc)_2/KOH$ -MeOH yields the corresponding α -hydroxy-dimethyl acetal.¹ In this transformation \neg OMe plays the role of an external nucleophile.

We now show that an o-hydroxy group in various substi-







tuted o-hydroxyacetophenones acts analogously as an intramolecular nucleophile in the reductive cleavage of the C-I bond [(A) \rightarrow (B), Scheme 1]. A series of substituted o-hydroxyacetophenones (1a-d) were treated with excess of PhI(OAc)₂ in KOH-MeOH to yield the corresponding



Reagent: i, $PhI(OAc)_2$, KOH-MeOH, 0 °C, then raised to room temperature.



Reagent: i, dilute H₂SO₄, heat.



Scheme 2. Reagent: i, PhI(OAc)₂, KOH-MeOH.

coumaran-3-ones (2a-d). † Acid treatment of (2d) yielded a mixture of aurone (3) and isoaurone (4) in 60% yield as a 1:1 mixture which was separated by t.l.c.‡ A mechanism for the

† (2a), 20%, oil, i.r. (neat): 1740 cm⁻¹; ¹H n.m.r. δ: (CDCl₃) 3.5 (s, 6H, OCH₃), 6.68-7.7 (m, 4H) [the ¹H n.m.r. spectrum of (2a) has been reported: 3.54 (OCH₃); S. Antus E. Baitz-Gács, F. Boross, M. Nogradi, and A. Solyom, Liebigs Ann. Chem., 1980, 1271]; m/z 194(66%) M^+ , 163(71) M^+ – OCH₃, 166(59) M^+ – CO, 120(23) M^+ – C(OCH₃)₂, 121 (100) M^+ – [C(OCH₃)(OCH₂)]. (**2b**), 35%, oil, i.r. (neat): 1730 cm⁻¹; d: (CDCl₃) 1.55 (s, 3H, CH₃), 3.26 (s, 3H, OCH₃), and 6.9–7.8 (m, 4H); m/z 178(38) M⁺, 147(14) M⁺-OCH₃, 150(21) M^+ -CO, 148(33) M^+ -CH₂O, 91(100). (2c), 21%, m.p. 59–60 °C, i.r. (Nujol): 1730 cm⁻¹; δ : (CDCl₃) 2.33 (s, 3H, CH₃), 2.5 (s, 3H, CH₃), 3.4 (s, 6H, OCH₃), 6.6 (s, 2H); m/z 222(44) M⁺, 191(43) M^+ - OCH₃, 192(10) M^+ - CH₂O, 148(14) M^+ - C(OCH₃)₂, 132(100). (2d) was obtained from (1d), 40%, oil, i.r. (neat): 1725 cm⁻¹; δ : (CDCl₃) 3.15 (s, 5H, CH₂ and OCH₃), 6.63-7.4 (m, 9H, aromatic); m/z 254(16) M^+ , 223(2) M^+ -OCH₃, 163(100) M^+ -CH₂Ph. The conversion of (1a) and (1c) into (2a) and (2c), respectively, is 30% and (1b) and (1d) into (2b) and (2d), respectively is 50% using equimolar amounts of PhI(OAc)₂ and ketone. The conversion is not increased with 2 or 3 equiv. of PhI(OAc)₂ relative to the ketone. Yields are of the pure isolated compounds by chromatography.

‡ Aurone (3), i.r. (CHCl₃): 1710 cm⁻¹; ¹H n.m.r. δ : (CDCl₃) 6.9 (s, C=CH); ¹³C n.m.r. δ : (CDCl₃) 111.19 (s, C=CH), 183.5 (C=O); *m/z* 222(100) *M*⁺, 120(34) *M*⁺-C=CHPh. Isoaurone (4), i.r. (CHCl₃): 1780 cm⁻¹, δ : (CDCl₃) 7.86 (s, C=CH); ¹³C n.m.r. δ : (CDCl₃) 133.6 (s, C=CH), 170 (C=O); *m/z* 222(100) *M*⁺, 194(39) *M*⁺-CO. ¹H, ¹³C N.m.r. and i.r. data for (3) and (4) are in excellent agreement with the data reported for 6-methoxyaurone and 6-methoxyisoaurone (ref. 2).



reactions $(1a-d) \rightarrow (2a-d)$, illustrated for $(1a) \rightarrow (2a)$, is shown in Scheme 2.

Coumaran-3-one $(7)^3$ was separately subjected to the reaction conditions and yielded (2a) in 50% yield. Intermediate (5) is based upon the general mechanism [viz. intermediate (A)] presented in Scheme 1. Intramolecular displacement with reductive elimination $[(5) \rightarrow (7)]$, a 5-exo-tet process, is stereoelectronically favourable.⁴ Alternative intermolecular attack by MeO⁻ $[(5) \rightarrow (6)]$ is possible, but $[(6) \rightarrow (7)]$ is stereoelectronically unfavourable.§

Hyperiodination $[(7) \rightarrow (8)]$, bimolecular reductive displacement $[(8) \rightarrow (9)]$, followed by the same sequence, yields (2a). This pathway also is considered to occur for (1b-d) \rightarrow (2b-d).

The formation of aurone (3) from (2d) results from acid-catalysed loss of MeOH. Isoaurone (4) is a rearrangement product which may result from a phenonium ion type intermediate (11).

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References

- R. M. Moriarty, H. Hu, and S. C. Gupta, *Tetrahedron Lett.*, 1981, 22, 1283; R. M. Moriarty, L. S. John, and P. C. Du, J. Chem. Soc., Chem. Commun., 1981, 641; R. M. Moriarty, S. C. Gupta, H. Hu, D. R. Berenschot, and K. B. White, J. Am. Chem. Soc., 1981, 103, 686; R. M. Moriarty and H. Hu, *Tetrahedron Lett.*, 1981, 22, 2747; R. M. Moriarty and K. C. Hou, *ibid.*, 1984, 25, 691; in this paper the advantage of using o-iodosylbenzoic acid in this oxidation reaction is described.
- 2 T. I. Gray, A. Pelter, and R. S. Ward, Tetrahedron, 1979, 35, 2539.
- 3 K. Fries and W. Pfaffendorf, Chem. Ber., 1910, 43, 212.
- 4 J. E. Baldwin, J. Chem. Soc., Chem. Commun., 1976, 738.
- 5 G. Stork, L. D. Cama, and D. R. Coulson, J. Am. Chem. Soc., 1974, 96, 5268; G. Stork and J. F. Cohen, *ibid.*, p. 5270.

§ Stork *et. al.* (ref. 5) have demonstrated convincingly that S_{N2} ring-opening of oxiranes requires a colinear arrangement of the nucleophile and C–O bond undergoing cleavage. This stereoelectronic effect is not met in (6) \rightarrow (7) even though an entropic advantage would exist in this intramolecular process. Both the favoured (5) \rightarrow (6) and unfavoured (6) \rightarrow (7) transformations are implicit in Eschenmoser's demonstration of the necessity for colinearity of reacting groups in intramolecular S_N2 processes (L. Tenud, S. Faroog, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, 1970, 53, 2059).